

# Massless Dirac fermions in epitaxial graphene on Fe(110)

A. Varykhalov, J. Sánchez-Barriga, P. Hlawenka, O. Rader

*Helmholtz-Zentrum Berlin für Materialien und Energie,  
Elektronenspeicherring BESSY II, Albert-Einstein-Straße 15, 12489 Berlin, Germany*

Graphene grown on Fe(110) by chemical vapor deposition using propylene is investigated by means of angle-resolved photoemission. The presence of massless Dirac fermions is clearly evidenced by the observation of a fully intact Dirac cone. Unlike Ni(111) and Co(0001), the Fe(110) imposes a strongly anisotropic quasi-one-dimensional structure on the graphene. Certain signatures of a superlattice effect appear in the dispersion of its  $\sigma$ -bands but the Dirac cone does not reveal any detectable superlattice or quantum-size effects although the graphene corrugation is twice as large as in the established two-dimensional graphene superlattice on Ir(111).

PACS numbers: 73.22.Pr, 79.60.Dp

The interfaces of graphene with ferromagnetic transition metals and the resulting electronic structure will be crucially important for the implementation of graphene in spintronics. Spin filter properties have been predicted for the epitaxial graphene/Ni(111) interface.[1, 2] Effective spin filtering requires hybridization between the exchange-split  $3d$ -bands of the substrate and the  $\pi$ -bands of graphene. This requirement as well as epitaxial growth are fulfilled in the graphene/Ni(111) and graphene/Co(0001) systems which have been widely studied in recent years both experimentally [3–5] and theoretically. [1, 2, 7, 8]

It has, however, been believed that the characteristic linear dispersion of Dirac fermions cannot exist in graphene/Ni(111) and graphene/Co(0001) due to the exceptionally strong breaking of sublattice symmetry of graphene as a result of its chemisorption in the *top-fcc* geometry. [9, 10] In this case, the opening of a band gap at the Dirac point is expected. We have recently examined the electronic structure of these systems by angle-resolved photoemission (ARPES) and discovered that the linear bands of Dirac fermions are neither destroyed by electronic hybridization between graphene and Ni or Co nor by the sublattice asymmetry of graphene. [11] On the contrary, density-functional-theory study has shown that the effect of sublattice symmetry breaking becomes compensated by hybridization-induced charge transfer so that the Dirac cones are preserved. [11]

While graphene on Ni(111) and Co(0001) have extensively been investigated, there are almost no reports about graphene on Fe surfaces, despite the larger magnetic moment of Fe. More detailed studies could also become important in the context of extrinsic carbon magnetism. The lack of investigations is possibly related to difficulties of graphene preparation on Fe. Indeed, our experience shows that chemical vapor deposition (CVD) of hydrocarbons at the parameters typical for Co and Ni substrates leads to the formation of iron surface carbide instead of graphene. A rare successful example has been the creation of a graphene/Fe(111) interface by intercalation of Fe between graphene and Ni(111). [6, 12] The

intercalated Fe films are ultrathin (a few monoatomic layers) and ARPES spectra have been reported in normal emission ( $\bar{\Gamma}$ ).[6, 12]

A breakthrough in the fabrication of graphene on Fe surfaces has recently been reported. Vinogradov et al. [13] found that the formation of iron carbide can be avoided in favor of graphene growth by significantly rising the partial pressure of carbon-containing molecules during the CVD procedure. Ref. 13 has demonstrated the formation of a high-quality graphene layer on Fe(110) with pronounced quasi-1D moiré pattern emerging from different lattice symmetries of graphene and the (110)-surface of bcc Fe. Graphene/Fe(110) has extensively been characterized by low-energy electron diffraction (LEED), scanning tunneling microscopy, core-level photoemission, and x-ray absorption spectroscopy but not by measurements of the band structure.[13] The band dispersions in 1D-modulated layers with a lateral periodicity of a few nanometers can be subject to lateral quantization [14–16] which is particularly interesting in the case of graphene.[17–19]

In the present paper, we study the band structure of graphene synthesized on Fe(110) in detail. The experimental data have been acquired by means of ARPES. Neither overview measurements of the electronic structure of graphene/Fe nor high-resolution data of the  $\pi$ -band in the vicinity of  $\bar{K}$ -point of the Brillouin zone of graphene, reveal any significant differences to the cases of graphene on Ni(111) and Co(0001).[11] The ARPES measurements demonstrate a fully intact Dirac cone at the  $\bar{K}$ -point also in graphene on Fe(110). The  $\sigma$ -bands reveal faint replicas which indicate an *umklapp* process due to 1D-modulation of graphene/Fe(110) but no significant quantum-size effects are revealed in the dispersion of the  $\pi$ -band.

The Fe(110) has been prepared as 40-monolayer film of Fe deposited and annealed on top of W(110). Graphene was fabricated by CVD of propylene as described in Ref. 13. The structural quality of the Fe(110) layer and of the synthesized 1D-modulated graphene were tested by LEED and photoemission. ARPES measurements have been conducted at the UE112-PGM2a beamline of

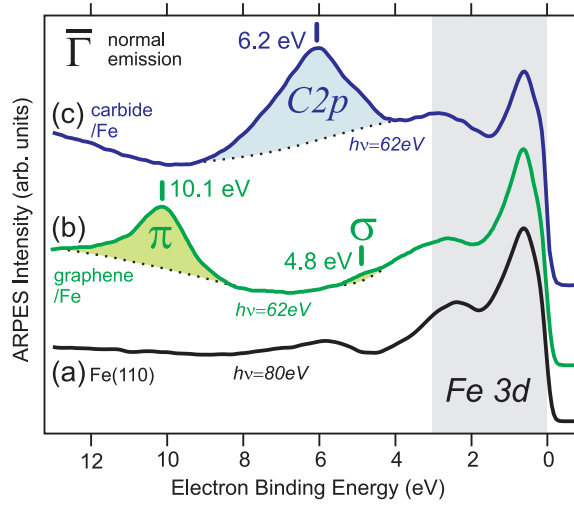


FIG. 1: Normal emission valence band spectra of (a) bare Fe(110) grown on W(110), (b) Fe(110) with graphene, (c) Fe(110) with surface carbide.

BESSY II using the end station ARPES I<sup>2</sup>. A photon energy of  $h\nu=62$  eV and linear (mixed s+p) light polarization have been used. Measurements have been performed at room temperature. Figure 1 shows valence band spectra of Fe(110) before [Fig. 1(a)] and after [Fig. 1(b)] synthesis of the graphene overlayer. Spectra were measured at the  $\bar{\Gamma}$ -point of the Brillouin zone ( $k_{\parallel}=0$  Å<sup>-1</sup>). The formation of graphene is evidenced by an intense photoemission peak of the  $\pi$ -band at 10.1 eV binding energy as well as a small peak corresponding to  $\sigma$ -bands at 4.8 eV. It is worthwhile noting that the binding energy of the  $\pi$ -band at  $\bar{\Gamma}$  is very close to that for graphene on Ni(111) and Co(0001) (Ref. 11) indicating that the chemical interaction of graphene with Fe is strong, exactly as with Ni and Co. For the purpose of comparison, Fig. 1(c) shows a valence band spectrum of fully carbidized Fe(110) which is typically obtained when CVD is performed at a low partial pressure of hydrocarbons. The iron surface carbide is identified by a very broad peak at  $\sim 6.2$  eV which does not disperse with the emission angle (wavevector  $k_{\parallel}$ ).

Figure 2(a) displays in color scale the overall band structure of graphene on Fe(110) sampled along  $\bar{\Gamma}-\bar{K}$  and  $\bar{\Gamma}-\bar{M}$  directions of the graphene Brillouin zone (sketched in the insets). Figures 2(b) and 2(c) additionally emphasize the dispersions by presenting ARPES spectra for different emission angles. One sees that the structural quality of the graphene is high, as no significant contribution from rotational domains occurs (such appears for graphene/Co(0001) [11]). Besides faint additional bands of  $\sigma$ -type near the  $\bar{\Gamma}$ -point (see further below) the band structure is almost identical to that of graphene on Ni and Co. [11] It is also clearly seen that the  $\pi$ -band disperses through the  $\bar{K}$ -point of the Brillouin zone without any significant distortion (see Figs.

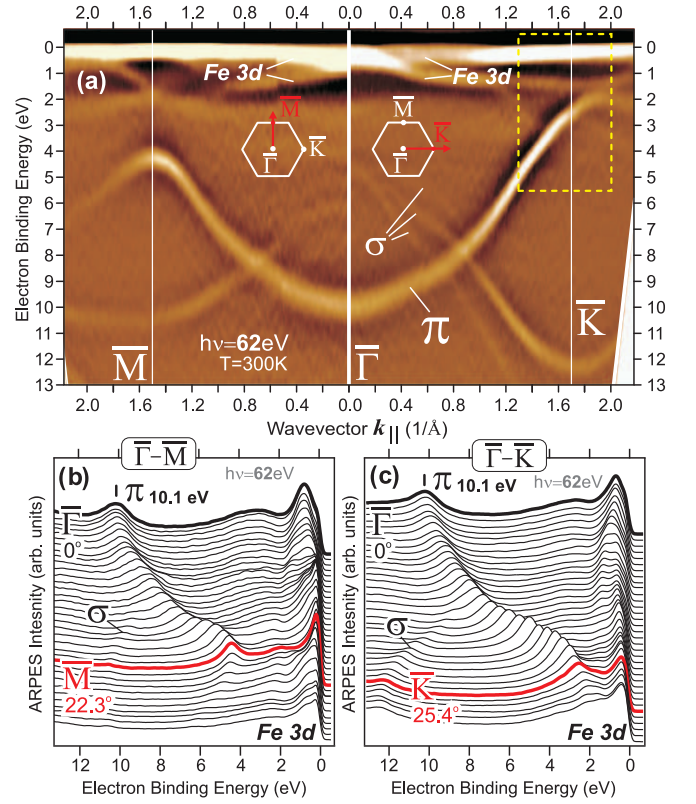


FIG. 2: (a) Overall band structure of graphene on Fe(110) sampled by ARPES along  $\bar{\Gamma}-\bar{K}$  and  $\bar{\Gamma}-\bar{M}$  directions of the surface Brillouin zone in a color-scale representation. (b) Dispersion along  $\bar{\Gamma}-\bar{M}$  as ARPES spectra. (c) Dispersion along  $\bar{\Gamma}-\bar{K}$  as ARPES spectra.

3(a) and 3(c) which zoom the area marked in Fig. 2(a) by a yellow dashed frame).

To investigate the behavior of the  $\pi$ -band at the  $\bar{K}$ -point more in detail, we have sampled its dispersion along the direction  $\perp\bar{\Gamma}-\bar{K}$ , where both sides of the conical dispersion are seen. [11, 20] The result is displayed in Fig. 3(b) and emphasized through the second derivative of the photoemission intensity over the energy. Raw ARPES data are displayed in Fig. 3(d) as stacked spectra. One clearly sees an intact Dirac cone with intense Dirac crossing point. The Dirac point is located at at 2.62 eV binding energy which manifests a significant  $n$ -doping of graphene. The experimental dispersion near the  $\bar{K}$ -point perfectly fits with the linear bands of ideal graphene obtained from the tight-binding model [21] [yellow dashed lines in Fig. 3(b)] after a corresponding energy shift. The observation of the intact Dirac cone clearly indicates the presence of massless Dirac fermions in graphene on Fe(110). Similarly to the case of graphene on Ni and Co, [11] the folding of the  $\pi$ -band at lower binding energy due to hybridization with Fe  $3d$ -bands and occurrence of a hybridization gap are observed.

The direction  $\perp\bar{\Gamma}-\bar{K}$  along which the dispersions from Fig. 3(b) has been measured corresponds to electrons

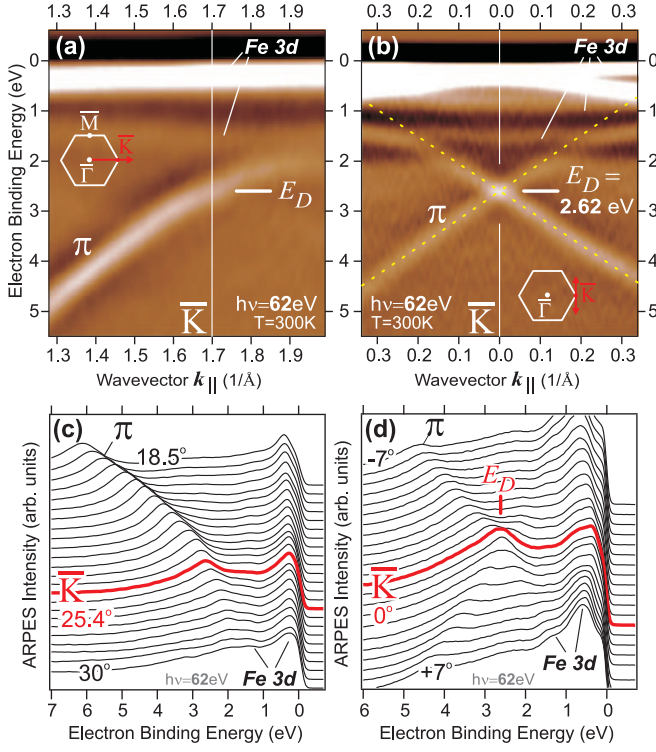


FIG. 3: Characterization of graphene/Fe(110) by high-resolution ARPES. (a) Dispersion of the  $\pi$ -band near the  $\bar{K}$ -point along  $\bar{\Gamma} - \bar{K}$ . (b) Intact Dirac cone revealed in the dispersion of the  $\pi$ -band in the  $\perp \bar{\Gamma} - \bar{K}$  direction. ARPES data in (a) and (b) are presented as second derivative over the energy. Raw data corresponding to (a) and (b) are displayed as spectra in (c) and (d), respectively.

propagating perpendicularly to the quasi-1D stripes of the graphene moiré on Fe(110). It is interesting that the Dirac cone, having proven sensitive to superlattice effects, [22, 23] exhibits no features which can be associated with any effects of superlattice of lateral quantization (e.g. band replicas or energy gaps). This is rather surprising since the amplitude of the structural corrugation of the 1D graphene moiré determined as 0.6-0.9 Å by scanning tunneling microscopy and density-functional theory in Ref. 13 is at least two times larger than that of graphene/Ir(111) for which moiré-induced quantum-size effects are very pronounced. [22–24]

The only signature of quantum-size effects was found in the  $\sigma_{2,3}$ -band of graphene near the center of the SBZ and along  $\bar{\Gamma} - \bar{K}$  direction. The effect is weak and can only be observed in the second derivative of the ARPES signal. Measured dispersions of  $\sigma_{2,3}$ -bands are zoomed in Fig. 4(a), Fig. 4(b) displays the extracted band structure. Faint *umklapp*-like replicas displaced by  $\Delta k = \pm 0.33 \text{ \AA}^{-1}$  from  $\bar{\Gamma}$  are seen. The real-space periodicity  $D = \frac{2\pi}{\Delta k}$  corresponding to  $\Delta k$  is about 16 Å, which differs by far from the periodicity of quasi-1D graphene stripes reported in Ref. 13 ( $\sim 40 \text{ \AA}$ ). However, the direction  $\bar{\Gamma} - \bar{K}$  along

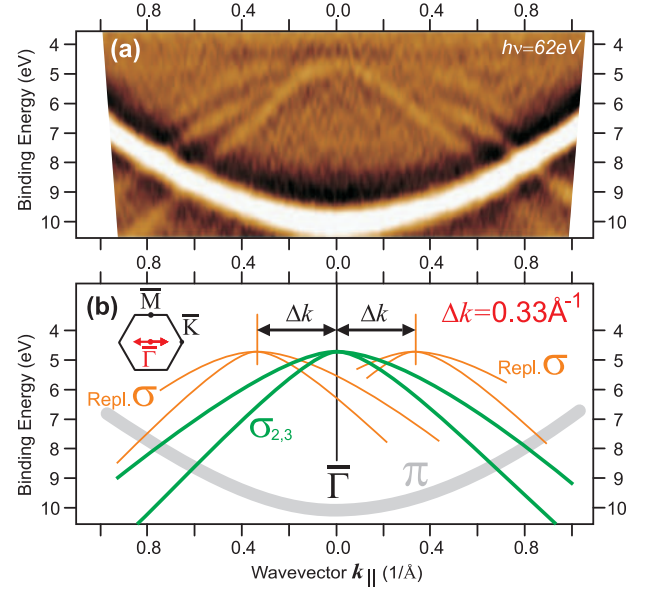


FIG. 4: (a) High-resolution measurements of the  $\sigma$ -band dispersion near the  $\bar{\Gamma}$ -point. The second derivative over the energy is shown. Faint replicas displaced by  $\Delta k \sim \pm 0.33 \text{ \AA}^{-1}$  from  $\bar{\Gamma}$  are seen. (b) Band structure of replicas extracted from ARPES data shown in (a).

which the dispersion in Fig. 4(a) was measured is the direction *along* the stripes, and, in principle, should not demonstrate any quantization effects. Ref. 13 has shown that the nanostructures of the graphene moiré on Fe(110) also possess a complex longitudinal wave-like pattern with a periodicity of  $\sim 19 \text{ \AA}$ . This value fits much better with the extracted  $D = 16 \text{ \AA}$  and suggests that the observed replication of  $\sigma$ -bands is *umklapp* emerging along the stripes due to the wave-type pattern. The question why no *umklapp*-induced replicas can be observed for the Dirac bands from Figs. 3(a) and 3(b) can be a subject for theoretical studies, since it has been shown that  $\pi$ - and  $\sigma$ -states must be equally sensitive to external superpotentials and superstructural corrugations. [25]

In summary, we have grown graphene on Fe(110) according to the method proposed by Vinogradov et al. [13] and characterized its electronic structure by angle-resolved photoemission. The obtained results are very similar to the band structures of graphene on Ni(111) and Co(0001) established in our earlier investigation. [11] Near the  $\bar{K}$ -point of the surface Brillouin zone the  $\pi$ -band of graphene on Fe(110) reveals a significant *n*-doping, a fully intact Dirac cone and pronounced electronic hybridization with the *3d*-bands of the ferromagnetic Fe substrate. Surprisingly, we did not observe any measurable quantum-size effects in the conical dispersion of Dirac fermions despite the quasi-1D moiré pattern of graphene on Fe(110) and weak signatures of *umklapp* in its  $\sigma$ -bands.

Acknowledgments. This work was supported by SPP

- 
- [1] V. M. Karpan, G. Giovannetti, P. A. Khomyakov, M. Talanana, A. A. Starikov, M. Zwierzycki, J. van den Brink, G. Brocks, P. J. Kelly, *Phys. Rev. Lett.* 99, 176602 (2007).
- [2] V. M. Karpan, P. A. Khomyakov, A. A. Starikov, G. Giovannetti, M. Zwierzycki, M. Talanana, G. Brocks, J. van den Brink, P. J. Kelly, *Phys. Rev. B* 78, 195419 (2008).
- [3] A. Varykhalov, J. Sánchez-Barriga, A. M. Shikin, C. Biswas, E. Vescovo, A. Rybkin, D. Marchenko, O. Rader, *Phys. Rev. Lett.* 101, 157601 (2008).
- [4] A. Varykhalov, O. Rader, *Phys. Rev. B* 80, 035437 (2009).
- [5] Yu. S. Dedkov, M. Fonin, U. Rüdiger, C. Laubschat, *Phys. Rev. Lett.* 100, 107602 (2008).
- [6] M. Weser, E. N. Voloshina, K. Horn, Yu. S. Dedkov, *Phys. Chem. Chem. Phys.* 13, 7534 (2011).
- [7] G. Bertoni, L. Calmels, A. Altibelli, V. Serin, *Phys. Rev. B* 71, 075402 (2005).
- [8] E. N. Voloshina, A. Generalov, M. Weser, S. Böttcher, K. Horn, Yu. S. Dedkov, *New J. Phys.* 13, 113028 (2011).
- [9] Y. Gamo, A. Nagashima, M. Wakabayashi, M. Terai, C. Oshima, *Surf. Sci.* 374, 61 (1997).
- [10] D. Eom, D. Prezzi, K. T. Rim, H. Zhou, M. Lefenfeld, S. Xiao, C. Nuckolls, M. S. Hybertsen, T. F. Heinz, G. W. Flynn, *Nano Lett.* 9, 2844 (2009).
- [11] A. Varykhalov, D. Marchenko, J. Sánchez-Barriga, M. R. Scholz, B. Verberck, B. Trauzettel, T. O. Wehling, C. Carbone, O. Rader, *Phys. Rev. X* 2, 041017 (2012).
- [12] Yu. S. Dedkov, M. Fonin, U. Rüdiger, C. Laubschat, *App. Phys. Lett.* 93, 022509 (2008).
- [13] N. A. Vinogradov, A. A. Zakharov, V. Kocovski, J. Ruzs, K. A. Simonov, O. Eriksson, A. Mikkelsen, E. Lundgren, A. S. Vinogradov, N. Mårtensson, A. B. Preobrajenski, *Phys. Rev. Lett.* 109, 026101 (2012).
- [14] A. Mugarza, J. E. Ortega, *J. Phys. Condens. Matter*, 15, S3281 (2003).
- [15] A. Mugarza, A. Mascaraque, V. Repain, S. Rousset, K. N. Altmann, F. J. Himpsel, Yu. M. Koroteev, E. V. Chulkov, F. J. García de Abajo, J. E. Ortega, *Phys. Rev. B* 66, 245419 (2002).
- [16] A. Varykhalov, O. Rader, and W. Gudat, *Phys. Rev. B* 72, 115440 (2005).
- [17] M. I. Katsnelson, K. S. Novoselov, and A. K. Geim, *Nat. Phys.* 2, 620 (2006).
- [18] V. V. Cheianov and V. I. Falko, *Phys. Rev. B* 74, 041403(R) (2006).
- [19] T. Ando, T. Nakanishi, and R. Saito, *J. Phys. Soc. Jpn.* 67, 2857 (1998).
- [20] E. L. Shirley, L. J. Terminello, A. Santoni, F. J. Himpsel, *Phys. Rev. B* 51, 13614 (1995).
- [21] P. R. Wallace, *Phys. Rev. B* 71, 622 (1947).
- [22] I. Pletikosić, M. Kralj, P. Pervan, R. Brako, J. Coraux, A. T. N'Diaye, C. Busse, Th. Michely, *Phys. Rev. Lett.* 102, 056808 (2009).
- [23] J. Sánchez-Barriga, A. Varykhalov, D. Marchenko, M. R. Scholz, O. Rader, *Phys. Rev. B* 85, 201413 (2012).
- [24] E. Starodub, A. Bostwick, L. Moreschini, S. Nie, F. E. Gabaly, K. F. McCarty, E. Rotenberg, *Phys. Rev. B* 83, 125428 (2011).
- [25] D. Usachov, A. Fedorov, O. Vilkov, V. K. Adamchuk, L. V. Yashina, L. Bondarenko, A. A. Saranin, A. Grüneis, D. V. Vyalikh, *Phys. Rev. B* 86, 155151 (2012).